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Controlled Chemical Polymerization Method for Processing Conducting Polymers Part 2

Final Report

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Contract Number: W7707-032288/A

Contract Scientific Authority: Dr. Colin G. Cameron, (902) 427-1367

Defence R&D Canada – Atlantic

Contract Report
DRDC Atlantic CR 2005-130
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Canada

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106-02651/

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Abstract

Potential applications of conducting polymers have attracted considerable attention over the past two decades. However, poor processability has limited the widespread utilization of these materials. To overcome this problem, several approaches have been pursued for the production of soluble conducting polymers (*e.g.*, attaching bulky side chains to the polymer backbone). These methods have resulted in increased solubility; however the conductivity typically decreases significantly. In this report, we extend our proof of concept study that was originally demonstrated with a metastable mixture of monomer and oxidant to the formation of polythiophene. The approach allows facile processing of solutions (*e.g.*, casting, spin coating, air-brush and painting) followed by *in situ* polymerization. In addition, this work explores the ability of this approach for the formation of interpenetrating polymer networks (IPNs). Specifically, we have focused on the addition of a non-conducting polymer into the metastable mixture as a way to generate conducting polymers composites. Films obtained with this method were smooth, homogeneous and well-behaved. The production of composites addresses a second problem that has restricted industrial applications of conducting polymers: environmental stability. This new methodology could lead to new composite materials combining the electronic properties of conducting polymers with the robust properties of a tough polymer host.

Résumé

Les applications potentielles des polymères conducteurs ont suscité un intérêt considérable au cours des vingt dernières années. Toutefois, leur mauvaise transformabilité a limité une utilisation généralisée de ces matières. Afin de résoudre ce problème, plusieurs approches ont été envisagées pour produire des polymères conducteurs solubles (par exemple, lier des chaînes latérales encombrantes au squelette du polymère). Ces méthodes ont conduit à une solubilité accrue, mais aussi à une conductivité nettement moindre. Dans le présent rapport, on va au-delà de la validation de principe que nous avions démontrée en produisant du polythiophène à partir d'un mélange métastable de monomère et d'oxydant. Cette approche permet une transformation facile des solutions (par exemple moulage, application par centrifugation, peinture au pistolet et peinture) suivi d'une polymérisation *in situ*. De plus, dans le cadre du présent travail, on a étudié la possibilité de production de réseaux polymères interpénétrants en suivant cette approche. Plus particulièrement, on s'est concentré sur l'addition d'un polymère non conducteur au mélange métastable, comme moyen de produire des composites polymères conduc-

teurs. Les pellicules minces ainsi obtenues sont lisses, homogènes et ont un bon comportement. La production des composites s'addresse à un deuxième problème limitant les applications industrielles des polymères conducteurs : la stabilité environnementale. Les méthodes démontrés içi pourrait mener à de nouveaux matèriaux composites combinants les propriétés électroniques des polymères conducteurs et les propriétés robustes d'un hôte en polymère résiliant.

Executive summary

Background

There is a class of polymeric materials that share the common feature of a backbone with alternating single and double bonds. Among the striking features of these materials is that they can be made to become electrically conductive. Understandably, this has generated a lot of interest since both lightweight electrical conductors and materials with adjustable electronic characteristics would be potentially very useful. However, in the twenty-five years since their discovery, conducting polymers have found few industrial applications, most likely due to their inability to be processed using methods typically used in the plastics industry.

Principal Results

This second report marks the conclusion of a two-year study. The first report [1] introduced the principle of controlled growth polymerization by demonstrating processed films of polypyrrole and also interpenetrating polymer networks. Key results of this second phase include: (i) successful transposition of the polymerization protocol to a different system, (ii) a study of the relationship between conductivity and the concentrations of reagents, (iii) demonstration of composites of conducting polymers with thermoplastic polyurethanes, and (iv) an examination of the electrical properties of these composites at different loading levels and a preliminary investigation of the changes in the electrical properties when the composite is exposed to varying thermal environments.

Significance of Results

The successful demonstration of the protocol with two different polymer systems (polypyrrole and polythiophene) underlines the portability of this method; polypyrrole and polythiophene are among the top researched conducting polymers, and all other conducting polymers should be accessible by this approach. The production of conducting polymer composite materials is also significant. The combined electric properties of polypyrrole with the robust elastomeric properties of a polyurethane hint at future military possibilities in areas such as active camouflage and electromagnetic signals management.

Future Work

This project is now at its conclusion. Future work will see attempts to move this techology towards prototype device construction and proof-of-concept demonstrations. The dielectric properties of the composites will be studied further in the Emerging Materials section as part of our continuing interest in energy storage materials.

Michael S. Freund; 2005; Controlled Chemical Polymerization Method for Processing Conducting Polymers Part 2; DRDC Atlantic CR 2005-130; Defence R&D Canada – Atlantic.

Sommaire

Contexte

Il existe une classe de matières polymères possédant la caractéristique commune d'un squelette avec alternance de liaisons simples et de liaisons doubles. Ces matières se distinguent par le fait qu'on peut les rendre conductrice de l'électricité, parmi d'autres propriétés interessantes. De façon fort compréhensible, ceci a suscité un grand intérêt, puisque des conducteurs électriques légers et des matières avec des caractéristiques électroniques réglables pourraient potentiellement être très utiles. Toutefois, au cours des vingt-cinq années qui ont suivi leur découverte, les polymères conducteurs n'ont reçu que peu d'applications industrielles, probablement à cause de leur incapacité à être transformés au moyen des méthodes généralement utilisées dans l'industrie des matières plastiques.

Résultats Principaux

Ce deuxième rapport constitue la fin d'une étude de deux années. Le premier rapport a introduit les principes de contrôler la croissance du polypyrrole, démontrant des filmes en polypyrrole traités et aussi des réseaux interpénétrants de polymère. Parmi les résultats les plus importants de cette deuxième phase, on retrouve : (i) réussite de la transposition du protocole de polymèrization vers un système différent ; (ii) étude de la relation entre la conductivité et les concentrations des réactifs ; (iii) production de composites de polymères conducteurs et de polyuréthanes thermoplastiques ; (iv) étude des propriétés électriques de ces composites à différents niveaux de charge et étude préliminaire des modifications des propriétés électriques lorsque le composite est exposé à divers environnements thermiques.

Importance des Résultats

La mise en évidence de la pertinence du protocole pour deux systèmes polymères différents (polypyrrole et polythiophène) indique que cette méthode est transférable. Le polypyrrole et le polythiophène sont parmi les polymères conducteurs les plus étudiés, et tous les autres polymères conducteurs devraient pouvoir être étudiés en suivant cette approche. La production de matières composites, polymères, conductrices, est aussi d'importance. Les propriétés électriques du polypyrrole combinées aux propriétés élestomères du polyuréthane offrent des possibilités dans des domaines militaires, comme ceux du camouflage et de la gestion des signaux électromagnétiques.

Travaux Futurs

Le présent projet arrive maintenant à sa conclusion. Les prochains travaux constitueront à construire des prototypes basés sur cette technologie et à faire des validations du concept. Les propriétés diélectriques de ces composites seront étudiées plus en détail par la section des matières émergentes, faisant parti de nos études continuantes des matériaux pour le stockage de l'énergie.

Michael S. Freund; 2005; Controlled Chemical Polymerization Method for Processing Conducting Polymers Part 2; DRDC Atlantic CR 2005-130; R&D pour la défense Canada – Atlantique.

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1 Introduction

Potential applications of conducting polymers have attracted considerable attention over the past two decades. However, poor processability has limited the widespread utilization of these materials. To overcome this problem, several approaches have been pursued for the production of soluble conducting polymers (*e.g.*, attaching bulky side chains to the polymer backbone). These methods have resulted in increased solubility; however the conductivity typically decreases significantly. In this report, we extend our proof of concept study that was originally demonstrated with a metastable mixture of monomer (pyrrole) and oxidant (phosphomolybdic acid), to the formation of polythiophene. The approach allows facile processing of solutions (*e.g.*, casting, spin coating, air-brush and painting) followed by *in situ* polymerization. In addition, this work explores the ability of this approach for the formation of interpenetrating polymer networks (IPNs). Specifically, we have focused on the addition of a non-conducting polymer into the metastable mixture as a way to generate conducting polymers composites. Films obtained with this method were smooth, homogeneous and well-behaved.

2 Synthetic Background

A proof of concept study has demonstrated an approach that uses an easily processible mixture of monomer (pyrrole) and oxidant (phosphomolybdic acid), which rapidly polymerizes upon solvent evaporation [2]. The basic concept relies on the formation of a metastable mixture of oxidant and monomer by selecting an oxidant whose electrochemical potential is close to, but lower than, the monomer. This insures that the concentration of oxidized monomer, a radical cation, is low, thereby making the polymerization rate (a radical coupling reaction) slow. While the solutions are metastable, when concentrated (*i.e.*, upon solvent evaporation) the rate-limiting step becomes significantly faster, resulting in a rapid increase in the concentration of *n*-mers that have lower oxidation potentials. The increased concentration of radical cations, resulting from the more favourable thermodynamics, causes a further increase in the polymerization rate as the reaction proceeds. Theoretically, this approach is applicable to any system in this class of polymerization reactions as long as optimal conditions for monomer oxidation potential, oxidant formal potential and solvent evaporation can be found. Clearly the relative redox potentials of the monomer/oxidant, concentrations and nature of the solvent (volatility, polarity and hydrogen bonding donating and accepting ability).

3 Goal 1

To extend our polymerization approach to the production of polythiophene films.

3.1 Background

In our previous report [1] we demonstrated that polythiophene films can be chemically synthesized by spin coating mixtures containing bithiophene. The resulting films appear to exhibit similar morphologies, structures, and electrochemical behaviour as the electrochemically grown polythiophene films. However, an extra oxidizing step after the spin coating process was necessary to completely oxidize the polymer into its conducting state. In addition, significant differences in the quality of the films were observed as a function of the solvent used.

It was also found that the rate of the reaction of bithiophene with phosphomolybdic acid in acetonitrile indicates that increasing the concentration of phosphomolybdic acid in the polymerization mixture does in fact increase the rate of reaction. In this work we study both the effect of the concentration of phosphomolybdic acid and choice of solvent on the conductivity of the films.

3.2 Experimental Design

Upon completion of spin-coating the chemically prepared films, they were rinsed in acetonitrile to remove the unreacted material.

3.2.1 Method

The polymerization mixture for synthesizing spin-coated polythiophene consisted of 0.2 M of bithiophene in acetonitrile and 0.1 M of phosphomolybdic acid in acetonitrile. The chemically grown films were spin-coated with the following settings: 2000 RPM (2000 ramp) during 10 seconds. The films were then left to dry at room temperature for 40 minutes before being rinsed with acetonitrile then again left to dry before characterization. Polythiophene films were then prepared using the method above while varying the concentration of oxidant or monomer. For purposes of comparison, polythiophene films were grown electrochemically from a solution of 0.01 M of bithiophene in a 0.1 M of tetrabutylammonium hexafluorophosphate ($TBPF_6$) in acetonitrile, as electrolyte solution, at a scan rate of 0.1 $V\,s^{-1}$.

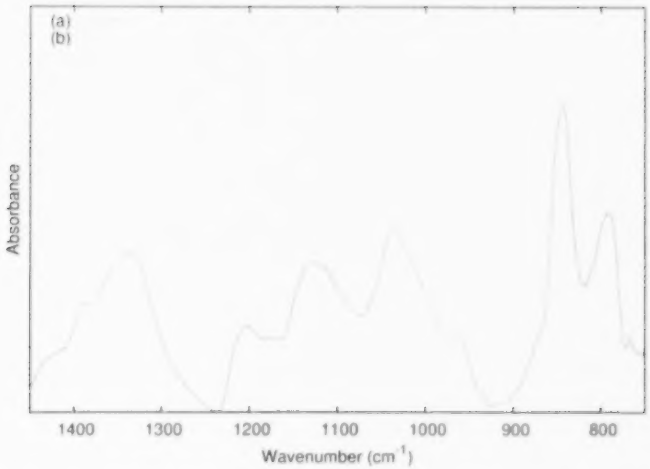


Figure 1: *FT-IR spectra of polythiophene (a) spin-coated on ITO vs. (b) electrochemically grown polythiophene on ITO substrate.*

3.3 Results and Discussion

In our previous report, the polymerization mixture for synthesizing spin-coated polythiophene consisted of 0.1M of bithiophene in acetonitrile and 0.05 M of phosphomolybdic acid in acetonitrile. The films produced were found to be in the reduced form, (the non-conducting state). As a result, an additional step to the spin-coating process was executed in order to chemically oxidize the films using 0.01 M solution of $FeCl_3$ in acetonitrile. The higher concentrations described herein has eliminated the need for this step.

In order to verify that polythiophene was indeed produced during spin-coating, FT-IR spectra of the films were studied and compared to the electrochemically grown film. The chemically grown and electrochemically grown films were analyzed with polarization modulated-infrared reflectance absorbance spectroscopy (PM-IRRAS). The absorption spectra of both chemically and electrochemically prepared films appear very similar (see Figure 1) and exhibit characteristic vibrations of polythiophene. The films absorbs at 1500 cm^{-1}, and 825 cm^{-1}, which corresponds with literature values for the absorption of films prepared by both methods [3, 4]. The peak at 825 cm^{-1} is representative of the aromatic C–H out of plane deformation. The characteristic peak positions associated with phosphomolybdic acid, (if present) would include a P–O stretch at 1065 cm^{-1}, M=O terminal at 963 cm^{-1}, M–O–M corner share at 867 cm^{-1}, and M-O-M edge share at 784 cm^{-1} [5, 6].

We also examined the effects of PMA concentration on the conductivity of the

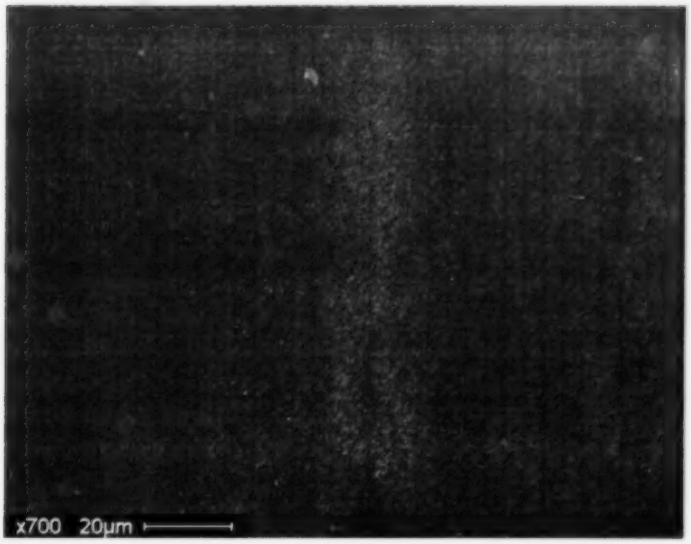


Figure 2: *Scanning electron micrograph of spin coated polythiophene films on glass substrate.*

resulting material. In one series of experiments, films were prepared by spin coating solutions containing a constant concentration of 0.2 M of bithiophene in acetonitrile while varying the concentration of phosphomolybdic acid from 0.1 M to 0.4 M in acetonitrile. In a second series, the concentration of phosphomolybdic acid was held constant at 0.25 M and the concentration of bithiophene varied between 0.25 M and 0.3 M. The resulting films were grey-green colour and no further oxidizing step was necessary.

Films prepared with the lower concentration of phosphomolybdic acid turned brown after a week. By increasing the concentration of phosphomolybdic acid in the mixture, the thickness of the films increased. This was determined by the difference in weight (the glass substrates before and after the spin coating process) the cross area of the glass slide and assuming 1.5 as the density of polythiophene ($\rho = 1.4 - 1.6$). Thicknesses of the films were in the range from 200 to 350 nm.

3.3.1 SEM Measurements

Scanning electron microscopy of the spin coated polythiophene films onto glass substrate demonstrated that they were smooth and pin-hole free at (see Figure 2). EDS analysis of the films indicate the presence of Mo, likely present as counter ions required for the oxidized conducting form of the film. As stated in our previous report, there is no evidence in the voltammetry, IR or UV-vis spectroscopy that the

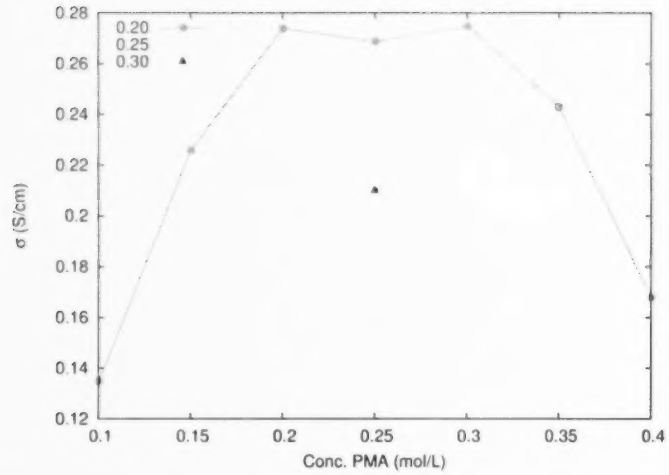


Figure 3: *Conductivity vs. concentration of oxidant (phosphomolybdic acid). The concentration of bithiophene was kept constant (0.2 M) unless otherwise indicated.*

Keggin structure of phosphomolybdic acid is retained in the film.

3.3.2 Conductivity

Conductivity measurements were performed using a four point probe device. Varying the relative concentration of phosphomolybdic acid in the reaction mixture resulted in variations in conductivity ranging from 0.02 $S\,cm^{-1}$ to 0.3 $S\,cm^{-1}$ (see Figure 3). The conductivity value reaches its maximum when the concentration of phosphomolybdic acid is between 0.2 M and 0.3 M, and then decreases. This is likely due to the fact that at high phosphomolybdic acid concentrations, the film becomes more porous due to the presence of excess acid, and at low concentrations, the polymer is not deposited as efficiently or not completely oxidized. This is supported by the observation that films with lower concentrations of phosphomolybdic acid appear thinner and the colour changes from grey-green to brown within a few days with a corresponding decrease in conductivity. For all the other films, the conductivity remained unchanged over the same time period.

Figure 3 also shows conductivity values obtained for varying the concentration of bithiophene while keeping the phosphomolybdic acid concentration constant. The conductivity values decrease significantly comparatively to those obtained in the first set of films. The lower conductivity values obtained under these conditions suggest that there was not enough phosphomolybdic acid to oxidize the polymer efficiently. The highest conductivity obtained using our method does not reach values reported in the literature on the order of 4–5 $S\,cm^{-1}$ [7]. This may be due to

Table 1: *Solvent physical properties*

Solvent	Polarity index	Dielectric constant
Isopropyl alcohol	3.9	19.92
Tetrahydrofuran*	4.0	7.58
Acetone	5.1	20.70
Methanol	5.1	32.70
Acetonitrile†	5.8	37.50

* solvent preferred for polypyrrole

† solvent preferred for polythiophene

the density of the polymer films, which should be explored in future work.

In our previous report we indicated that while THF was the solvent of choice for spin coating polypyrrole, acetonitrile was the preferred for polythiophene. We also reported that it was not possible to generate homogeneous films of polythiophene from THF or polypyrrole from acetonitrile. To further study the role of solvent on polymerization, the rate of the polymerization of polythiophene in solution was studied in several other solvents including, methanol, isopropanol, acetone and THF using UV-vis spectroscopy. Data obtained from UV-vis showed that it was not possible to obtain polythiophene in the presence of any of these solvents.

A similar study was performed to investigate the rate of polymerization of pyrrole in methanol, isopropanol, acetone and acetonitrile as solvents with the same unsuccessful results. These solvents were selected because of their closer polarity index values to those of THF and acetonitrile (see Table 1). Clearly polarity does not play a dominant role in the polymerization mechanism. Instead, it is possible that protic solvents somehow interfere in the reaction. It is also possible that THF interacts with the Keggin structure precluding interaction bithiophene, which may for some reason may be required. However, if this is the case, it is unclear why the lack of this sort of interaction between acetonitrile and the Keggin structure would impact the polymerization of pyrrole, which should not act as a Lewis base as is the case with thiophene. Further investigation of these interactions is warranted.

In order to investigate the role of solvent on the redox reactions involved in polymerization, the voltammetry of the monomers and polymer were determined. Neither polythiophene nor polypyrrole were generated in THF or methanol, which was consistent with the observations in the chemical polymerization. As seen in Table 2, no oxidation peak for the monomer was observed in THF with the exception of pyrrole and while oxidation peaks were observed in methanol, no evidence of a redox polymer was observed. This influence of solvent on the redox properties of the polymer was investigated by electrochemically synthesizing the polymer in acetonitrile and then observing its redox behaviour in the various solvents contain-

Table 2: *Peak potential values obtained for polypyrrole and polythiophene in the presence of different solvents.*

Monomer	Oxidation potential (V)			Polymer from*	CV Peak potential (V)		
	MeCN	MeOH	THF		MeCN	MeOH	THF
Thiophene	1.9	–	–	Thiophene	1.15	X	X
Bithiophene	1.05	1.3†	–	Bithiophene	1.12	0.8	X
Terthiophene	0.75	1.3†	–	Terthiophene	0.9	X	X
Pyrrole	1.0	1.1†	1.0	Pyrrole	1.2	1.19	1.2

* Polymer grown in acetonitrile

† Oxidation peak potential. Deposited material does not show redox activity

– Monomer oxidation not observed

X No peak potential observed

ing 0.1 M $TBPF_6$. As seen in Table 2, oxidation wave for polythiophene was only observed in acetonitrile and not in the presence of THF or methanol. These results indicate that the solvent interferes with the redox process of both the monomer and the polymer and may be the reason for why acetonitrile is required for the process. It does not explain why polypyrrole can be polymerized chemically in THF using our approach, although it is possible that the lower redox potential of phosphomolybdic acid does not result in side reactions or decomposition of polymer or polymer intermediates.

3.4 Summary

It has been demonstrated that by increasing the concentration of oxidant (phosphomolybdic acid) in the initial mixture it is possible to obtain conducting polythiophene films without the need of an extra oxidizing step of the final films. The films obtained have lower conductivities than those reported in the literature, which may be due to increased porosity associated with the Keggin structure present during polymerization. It was also found that solvent plays an important role in the polymerization process and must be taken into account when applying this approach to new systems.

4 Goal 2

To prepare interpenetrating polymer networks (IPNs) with the conducting polymer over a wider range of percent composition.

4.1 Background

In our previous report we have found that the formation of IPNs within existing polymer structures was hampered by the amount of oxidant that could be loaded into the polymer. For example, as the concentration of phosphomolybdic acid is increased, the degree of swelling of a latex sample decreased, resulting in essentially a constant concentration of phosphomolybdic acid in the film. While this resulted in an IPN, there was no facile means for tuning the relative amount of conducting polymer in the network. In this report, we use pellethane, a thermoplastic, provided by DRDC as the non-conducting matrix.

4.2 Experimental Design

4.2.1 Synthesis

The present methodology utilizes tetrahydrofuran to dissolve pellethane, a thermoplastic polymer, and pyrrole (monomer). The resulting solution can be mixed with a phosphomolybdic acid/THF solution. Subsequently, the final mixture can be spin coated on glass substrate and allowed to dry at room temperature for about 40 min. Films obtained using this approach were rinsed with MeOH to remove any unreacted material without re-dissolving the pellethane and allowed to dry at room temperature before characterization.

4.2.2 Method: Interpenetrating Network Protocol

Pellethane ($\approx$28 mg) was dissolved in 0.5 mL of THF resulting in a viscous solution. Pyrrole monomer (29 μL) was then added to the pellethane solution giving a 1:1 (w/w) ratio of thermoplastic-polymer to monomer. Separately, 0.3866 g of phosphomolybdic acid was dissolved in 0.5 mL of THF. Both the pellethane-monomer and oxidant solutions were then mixed together and immediately spin coated on the glass substrate. The films were then rinsed with MeOH, dried at room temperature and weighed. Furthermore, the amount of pyrrole was varied in order to obtain different polypyrrole loadings in the composite. The amount of phosphomolybdic acid was then adjusted to maintain a 2:1 molar ratio of monomer-oxidant in the final mixture, following the polymerization method described by Freund *et al.* [2]

4.3 Results and Discussion

The FTIR-ATR spectra of the pellethane and composite (1:1 pellethane:polypyrrole) are shown in Figure 1. The as received pellethane spectrum shows the characteristic peaks at 1220 cm^{-1} and 1108 cm^{-1} of polyurethanes as observed by Tanzi *et*

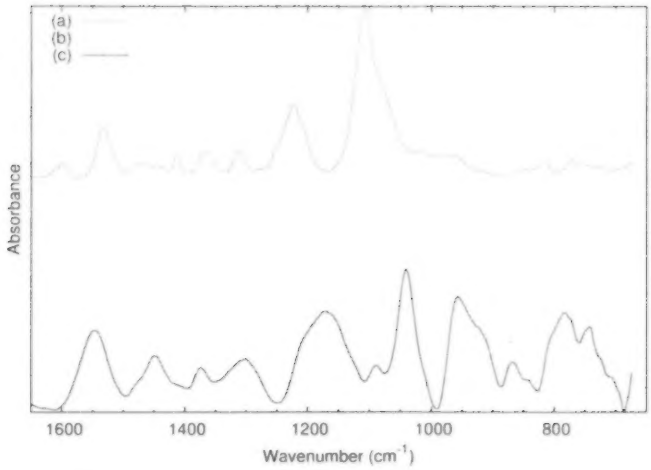


Figure 4: *FTIR-ATR spectra of (a) pellethane, (b) composite (1:1 pellethane:polypyrrole), and (c) pure polypyrrole.*

al. [8]. The spectra of the composite shows a characteristic peak at 1530 cm^{-1} that correspond to the C=C and C=N in-plane vibrations in the pyrrole structure [3, 9]. The peak at approximately 1310 cm^{-1} is attributed to the secondary amines C–N stretching. The peaks at 790 cm^{-1} and 913 cm^{-1} are a combination of a number of absorptions corresponding to NH_2 wag, symmetric C–N–C stretching and its deformation and appears to have shifted to 770 cm^{-1} and 950 cm^{-1} respectively, perhaps due to its interaction with the pellethane matrix.

SEMs of pure polypyrrole and pellethane spin coated films are shown in Figure 5. Polypyrrole films are very smooth and pin-hole free at high magnification as reported by Freund *et al.* [2]. In contrast pellethane films show a rougher, more porous surface (see Figure 7b) probably due to the formation of micro bubbles during the mixing process.

In the case of the composite films, no evidence of phase separation is observed in the SEM indicating a good mixture of polypyrrole and pellethane in the final composite material as shown in Figure 6.

AFM measurements were performed to further investigate morphology and to determine the thickness of the films. Using the weight by difference (before and after the film deposition) and the area of each glass slide, the thickness of the films was estimated to be on the order of 200 nm. Films were scrapped with a razor blade and the topography analyzed by AFM tapping mode (see Figure 7). Films were found to be on the order of 200 nm as calculated before.

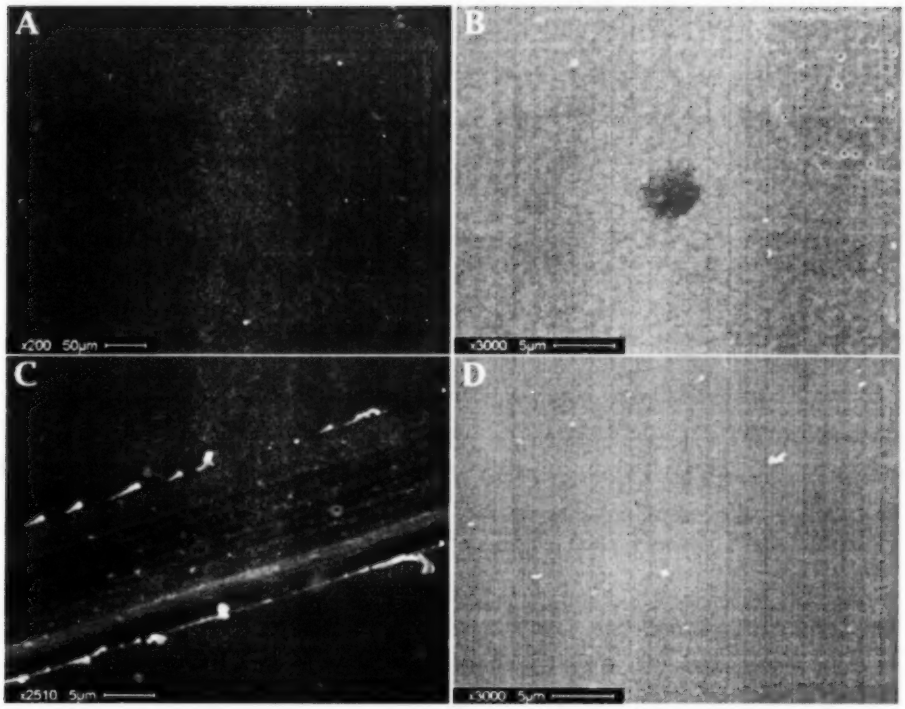


Figure 5: *SEM micrographs of spin coated (a,b) pellethane and (c,d) polypyrrole on glass substrate. Scratch in image c is intentional.*

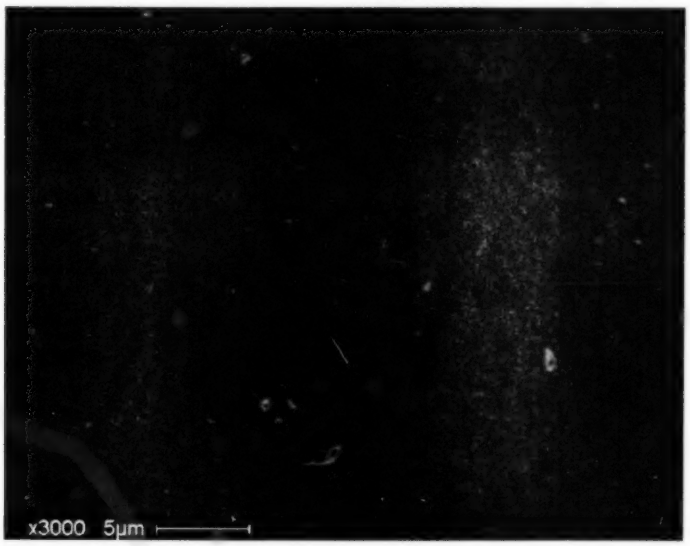


Figure 6: *SEM micrographs of the 50/50 composite.*

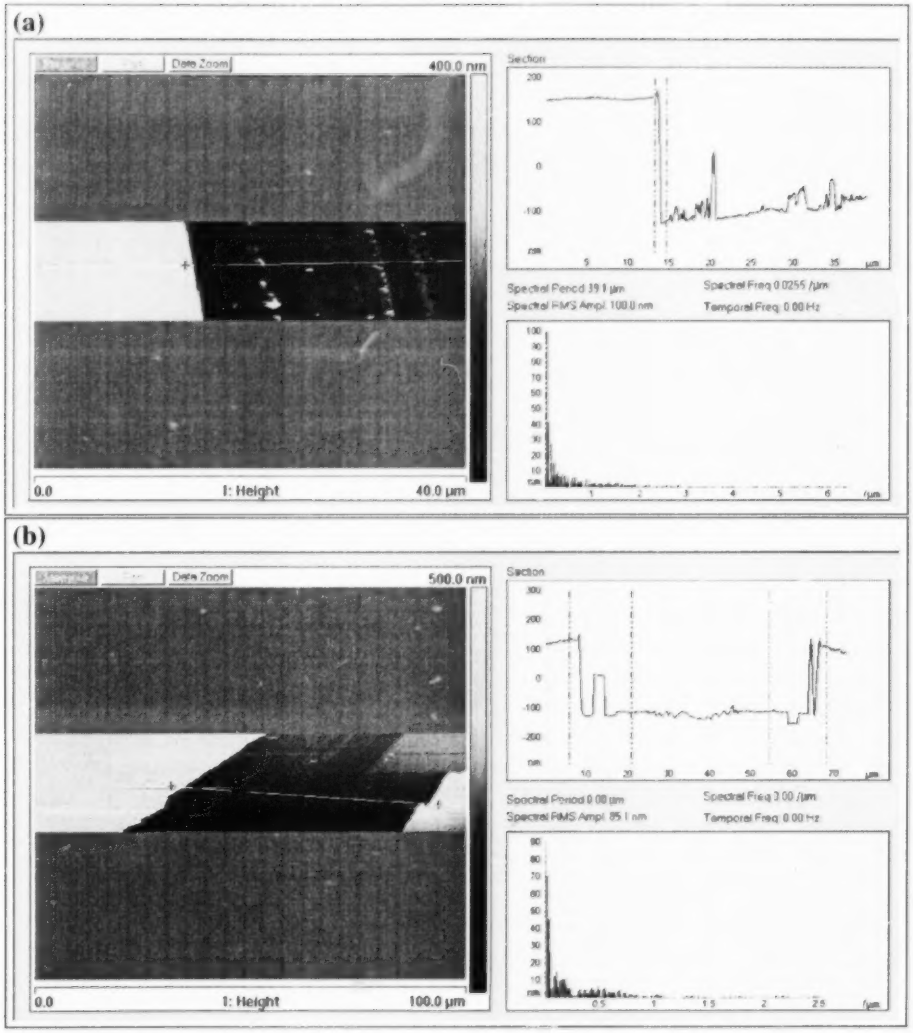
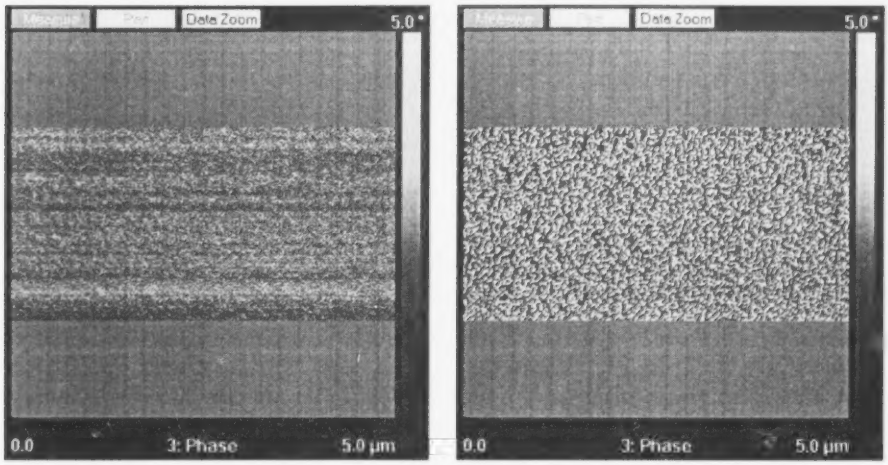


Figure 7: *AFM micrographs showing the thickness of (a) polypyrrole (b) composite.*

The morphology of the resulting films was also analyzed and compared to pure polypyrrole. While Figure 7 shows that the surface roughness is very small relative to the thickness of the films, phase images of pure polypyrrole and the composite shown in Figure 8 indicate similar surface structure on a sub-micron scale in both cases. The enhanced contrast in the phase images associated with the composite suggests that compositional differences may exist on this scale. These results suggest that the composite is relatively homogeneous with no major phase segregation.



(a) (b)

Figure 8: *AFM phase images of the topology of (a) polypyrrole and (b) 1:1 composite.*

4.3.1 Conductivities

Due to the nature of the composite, it was expected that it would exhibit percolation behaviour. Figure 9 shows the percolation threshold of conductivity for the polypyrrole-pellethane composite. When the polypyrrole content is lower than 5%, its conductivity was too low to measure with our equipment. In the range of 5–10% polypyrrole the conductivity increases markedly, reaching its maximum limit at around 30%. The percolation value was estimated from this plot to be near 8%. This percolation value is similar to that observed by Xie *et al.* [10] of about 6% and 12% for polypyrrole/ rubber and polypyrrole/chlorinated polyethylene composites respectively, and higher than that observed by Chakraborty et al. of about 3.5–5% for polypyrrole content in polypyrrole/poly(vinyl acetate) [11, 12].

Electrical conductivity of the composite was also measured as a function of temperature. Spin coated films were heated over a heating plate up to the reported melting-softening temperature of pellethane (225 °C) [13] and the conductivity was measured with the standard four point probe technique (see Figure 10). Thermal history of the pellethane appears to have an impact on the conductivity of the IPNs obtained. In the heating process the conductivity remains fairly level until it nears 200 °C, where it begins to decrease. The conductivity continues to decrease as it is cooled but stabilizes to a constant valued below 200 °C. These resistance changes may be due to changes in the contact points of the four point probe, however they do not reflect a major loss in conductivity.

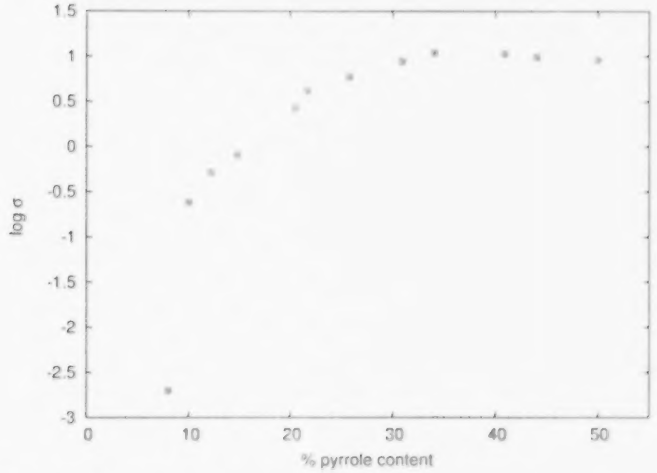


Figure 9: *Relationship between conductivity and polypyrrole content of the polypyrrole-pellethane composite.*

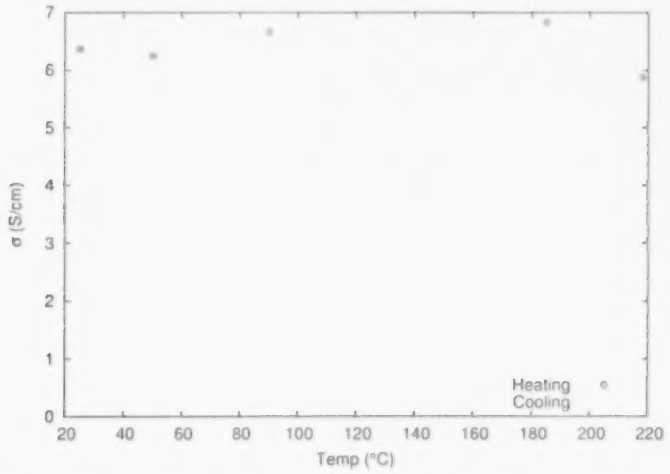


Figure 10: *Effect of Conductivity vs. Temperature for 44% content of polypyrrole in the composite.*

To further explore the temperature dependence of conductivity, the cross-sectional resistance of a free standing film was measured as a function of temperature. After spin coating a thin film on a glass substrate, the film was rinsed with MeOH and then left to soak in MeOH for 40 min. The film then easily peeled off at once from the glass substrate and could be transferred to an ITO coated electrode and left dry at room temperature. We found that only freshly made composite films could eas-

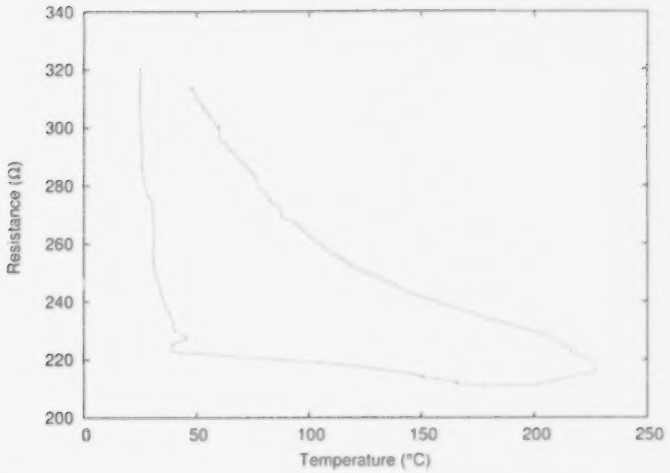


Figure 11: *Resistance as a function of temperature of a 1:1 composite in function of time (arrows indicate the heating direction).*

ily be removed from the glass substrate. Once the film has completely dried on the ITO surface, a bare ITO was positioned over the film (conducting surfaces were positioned face-to-face) at an angle of 90 °C. The ITO electrodes were then placed on a heating plate (compressed with light pressure) and temperature was increased step wise at a rate of 10 °C/min. Resistance was then measured as a function of time with a multimeter. The temperature was increased rapidly up to 50 °C followed of slowly increasing up to the melting-softening temperature. As seen in Figure 11, the resistance decreased with increasing temperature, returning to near its original value upon cooling. Once both ITO electrodes reached room temperature the upper ITO electrode was easily removed without any residual trace of the composite. No apparent damage was observed on the film or the ITO supporting the film. Interestingly, the change in resistance is different than that observed in the four point probe measurement and is more consistent with the temperature dependence of conductivity reported in the literature, where conductivity increases with increasing temperature.

4.4 Summary

PM-IRRAS data as well as the SEM and AFM micrographs indicate that an IPN is in fact produced. The percolation threshold of the final material is in the range of values reported in the literature for other systems involving polypyrrole. During the cycling of the temperature between 20 and 200 °C, there is no evidence of decomposition. All films including composite and pure conducting polymer have been

found to be in the order of 200 nm in thickness and after being soak in methanol it is possible to obtain free standing films of the composite films which provides an opportunity further characterization of its physical properties.

5 Conclusions

The polymerization approach utilizing metastable monomer/oxidant mixtures for in situ polymerization has been extended to the polythiophene system. This is an important breakthrough since this particular polymer is used in many emerging applications involving conducting polymers including in light emitting diodes and electrochromic devices. The work demonstrates that this approach is general and may be applied to other systems under the appropriate solvent/oxidant conditions. Further, this work demonstrates that the metastable mixtures can be used to create composite materials and IPNs thereby combining the conductivity of the polymer and the properties of other polymers. This was clearly demonstrated with pellethane, a polymer currently being studied by DRDC. Future work will characterize this composite as a potential high dielectric insulating material below its percolation threshold.

6 Experimental Details

6.1 Chemicals and Materials

The Phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40} \cdot x\,H_2O$, FW: 1825.24), Pyrrole (C_4H_5N, FW: 67.09), 2,2′-bithiophene ($C_8H_6S_2$, FW: 166.26), Tetrahydrofuran (THF, HPLC grade), Acetonitrile (CH_3CN, HPLC grade) and Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were obtained from Aldrich and used as received. Pellethane 2103-70A (Dow Corning) was generously provided from DRDC.

6.2 Instruments

6.2.1 Electrochemical Apparatus

All Cyclic voltammetric measurements were performed using a CH Instrument, CHI-660 workstation at room temperature. A three-electrode set up using a platinum coil auxiliary electrode, a Pt working electrode, and an $Ag/AgNO_3^-$ reference electrode. All measurements were performed using tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile as electrolyte.

6.2.2 Four point probe measurements

Four point probe measurements were performed using a four point probe device attached to a CHI-660 workstation controlled by a PC.

6.2.3 Scanning Electron Microscopy

Scanning Electron Microscopy data was collected using a SEM fitted with a Kevex 7000 EDS spectrometer that provides '3-D' images at high magnifications, BES and secondary-electron images. It has a 4-quadrant semiconductor BES detector.

6.2.4 FTIR measurements

FTIR measurements were recorded using a Thermo Nicolet Magna IR spectrometer at room temperature. PM-IRRAS data were collected from an accumulation of 300 interferograms at a resolution of 8 cm^{-1}. ITO as well as glass slides were positioned at 63° with respect to the detector. ATR spectra were collected from an accumulation of 100 interferograms at a resolution of 4 cm^{-1}.

6.2.5 UV-VIS measurements

UV-VIS measurements were collected at room temperature using a UV-VIS Chem Station Rev. A.09.01[76] from Agilent Technologies.

6.2.6 Atomic force microscopy

Tapping mode AFM images were obtained with a Veeco Nanoscope IV.

7 Symbols and Abbreviations

AFM Atomic force microscopy

BES Back electron scattering

EDS Energy dispersion (x-ray) spectroscopy

FTIR Fourier transform infrared

FTIR-ATR FTIR attenuated total reflectance

FW Formula weight

ITO Indium tin oxide; a glass slide coated with ITO

PM-IRRAS Polarization modulated-infrared reflectance absorbance spectroscopy

IPN interpenetrating polymer network

MeCN Acetonitrile

MeOH Methanol

SEM Scanning electron microscopy

$TBAPF_6$ Tetrabutylammonium hexafluorophosphate

THF Tetrahydrofuran

UV-vis Ultraviolet-visible spectroscopy

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Potential applications of conducting polymers have attracted considerable attention over the past two decades. However, poor processability has limited the widespread utilization of these materials. To overcome this problem, several approaches have been pursued for the production of soluble conducting polymers (*e.g.*, attaching bulky side chains to the polymer backbone). These methods have resulted in increased solubility; however the conductivity typically decreases significantly. In this report, we extend our proof of concept study that was originally demonstrated with a metastable mixture of monomer and oxidant to the formation of polythiophene. The approach allows facile processing of solutions (*e.g.*, casting, spin coating, air-brush and painting) followed by *in situ* polymerization. In addition, this work explores the ability of this approach for the formation of interpenetrating polymer networks (IPNs). Specifically, we have focused on the addition of a non-conducting polymer into the metastable mixture as a way to generate conducting polymers composites. Films obtained with this method were smooth, homogeneous and well-behaved. The production of composites addresses a second problem that has restricted industrial applications of conducting polymers: environmental stability. This new methodology could lead to new composite materials combining the electronic properties of conducting polymers with the robust properties of a tough polymer host.

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